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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : B32B 27/08, 27/36		A1	(11) International Publication Number: WO 95/34425
		(43) International Publication Date: 21 December 1995 (21.12.95)	
(21) International Application Number: PCT/US95/07508 (22) International Filing Date: 13 June 1995 (13.06.95) (30) Priority Data: 08/258,894                      13 June 1994 (13.06.94)                      US 08/333,154                      1 November 1994 (01.11.94)                      US (71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: DEGRASSI, Alfieri; P.O. Box 564, Pottsville, PA 17901 (US). FRYER, James, I.; 5 East Liberty, Schuylkill, PA 17972 (US). HITZEL, Andrew, G.; Road #4, Box 4027, Chesnut Street, Pottsville, PA 17901 (US). MATAS, Michael, S.; 19 North Second Street, St. Clair, PA 17970 (US). (74) Agent: CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: RETORTABLE, HIGH OXYGEN BARRIER POLYMERIC FILMS			
(57) Abstract  A polymeric film having superior oxygen barrier properties comprising at least five layers with at least one exterior layer comprised of polyester, one exterior layer selected from the group consisting of a polyester, an aliphatic polyamide, and an aliphatic/aromatic polyamide, an interior layer of ethylene vinyl alcohol copolymer or a blend of an ethylene vinyl alcohol copolymer and an aliphatic/aromatic polyamide, and a modified polyolefin adhesive layer between each exterior layer and the interior layer.			

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- 1 -

**RETORTABLE, HIGH OXYGEN BARRIER POLYMERIC FILMS****CROSS-REFERENCE TO RELATED APPLICATIONS**

5           This application is a continuation-in-part of application Serial No. 08/258,894, filed on June 13, 1994.

**BACKGROUND OF THE INVENTION**

10           **1. Field of the Invention:**

The present invention relates to polymeric films. More particularly, this invention relates to polymeric films having improved mechanical and gas barrier properties and capable of withstanding retorting.

15           **2. Description of the Prior Art:**

It is known in the art that polyolefin films, such as polyethylene and polypropylene, are common packaging materials because of their relatively high moisture resistance. However, these polyolefins also have a fairly high permeability to gases, including oxygen, so that if used alone, they are  
20           inadequate for packaging oxygen sensitive materials, such as food.

By contrast, polymers and copolymers of vinyl alcohol, such as those of polyvinyl alcohol and ethylene vinyl alcohol, have excellent resistance to gas permeation. However, both ethylene vinyl alcohol and polyvinyl alcohol films tend to lose this desirable property in the presence of moisture.  
25           Further, if the vinyl alcohol film is either exposed to high temperatures, such as approximately 240°C and above, or prolonged heat exposure, the film will form gels and decompose.

It is desirable to sandwich the substantially pure ethylene vinyl alcohol and polyvinyl alcohol polymers between polyolefin layers, but such  
30           polymers do not bond well to many polymer films. Furthermore, as the pure vinyl alcohol content of the interior layer is decreased by blending it with other polymers, its oxygen barrier properties likewise fall.

Also commonly used as a component in packaging films are polyamide polymers and copolymers as well as polyester polymers and  
35           copolymers. Examples of such prior art films containing polyamides are described in United States Patent Nos. 4,361,628, 4,254,169; 3,595,740; and 5,055,355. Examples of such prior art films containing polyesters are

- 2 -

described in United States Patent Nos. 4,999,229, 5,069,946, and 5,126,401 as well as in Japanese Patent Nos. 40-59353 A and 63-270140.

Another characteristic important to film laminates suitable for packaging materials is the ability to withstand the combination of heat and flexing to which it is often subjected during processes such as pasteurization or sterilization. However, many of the known laminates containing oxygen barrier layers are wholly unsuitable for such procedures in which they are subjected to temperatures between approximately 80°C to approximately 130° C. As a result of their low softening points, these known barrier laminates are unable to maintain their structural integrity. Other laminates which employ aluminum foil as the barrier component tend to develop pinholes during such procedures, thereby also rendering them unsuitable for such use since such pinholes cause a serious increase in oxygen permeability. Although this tendency can be controlled by sandwiching the foil between two biaxially oriented films, such laminates are inconvenient and costly to produce, and cannot be thermoformed.

Films capable of withstanding such exposure to heat and flexing are often referred to as "retortable". Retorting, as used herein, is defined as a process used to kill bacteria in which a material is subjected to higher temperature conditions, typically between 119 °C and 123 °C, than those typically employed for sterilization or pasteurization.

Retortable films comprised of two exterior layers of nylon sandwiching an ethylene vinyl alcohol copolymer layer modified with plasticizers such as nylon 6 and nylon 6/66 are disclosed in United States Patent No. 4,640,852 to Ossian.

It would be desirable to provide a film which has improved mechanical and gas barrier properties and which is capable of withstanding retorting conditions (e.g., temperatures in the range of about 119 °C to 123 °C).

#### **SUMMARY OF THE INVENTION**

In accordance with this invention, there is provided a retortable film comprised of:

- a) a first exterior layer comprised of polyester;
- b) a second exterior layer comprised of a polymer selected from the group consisting of aliphatic polyamides, aliphatic/aromatic polyamides, polyesters, and blends and copolymers thereof;

- 3 -

c) an interior copolymeric layer comprised of a component selected from the group consisting of ethylene vinyl alcohol and a blend of ethylene vinyl alcohol and an aliphatic/aromatic polyamide;

d) an adhesive layer positioned between each exterior layer and the interior layer.

The film of this invention exhibits one or more beneficial properties. Not only do the films exhibit excellent physical and oxygen barrier properties, but they also exhibit enhanced heat resistant properties to withstand the rigors of retorting conditions. Because the films of this invention possess the combination of these properties, they are especially suited for use in goods packaging applications.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and the accompanying drawings in which:

FIG. 1 is a cross-sectional view of a preferred structure of this invention having five co-extruded layers.

#### **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The basic form of the invention is shown by the co-extruded film of FIG. 1, which is generally designated 10. Film 10 has five layers: two exterior layers (12, 20); two adhesive layers (14, 18); and an interior layer (16). Layer 12 is formed from polyester, layer 20 is formed from a polymer selected from the group consisting of aliphatic polyamides, aliphatic/aromatic polyamides, polyesters, and blend and copolymers thereof. Preferably layer 20 is formed from polyester. Layer 16 is formed from either an ethylene vinyl alcohol copolymer or a blend of an ethylene vinyl alcohol copolymer and an aliphatic/aromatic polyamide. Layers 14 and 18 are formed from a modified polyolefin having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides. Preferably, the modified polyolefin is also copolymerized with vinyl acetate.

The film of this invention is not limited to the five layers 12, 14, 16, 18 and 20, provided that layer 16 is positioned between exterior layers 12 and 20. Thus, the film of this invention may include any number of additional layers in any position as, for example, the addition of other

- 4 -

polymeric film layers, and/or adhesive or tie layers. In the preferred embodiment of the invention, the films include only five layers 12, 14, 16, 18 and 20.

5 One or both of the exterior layers 12, 20 may be formed from linear or branched polyesters. The type of polyester is not critical and the particular polyester chosen for use in any particular situation will depend essentially on the physical properties and features, i.e. flexibility, hardness, and toughness, desired in the final film product. Thus, a multiplicity of linear thermoplastic polyesters having wide variations in physical properties are  
10 suitable for use in the film of this invention.

The particular polyester chosen for use can be a homo-polyester, a random or block copolyester or terpolymer, or mixtures thereof as desired. Many polyesters are generally prepared by the condensation of an organic dicarboxylic acid and an organic diol, and, therefore, illustrative examples of  
15 useful polyesters will be described hereinbelow in terms of these diol and dicarboxylic acid precursors.

Polyesters which are suitable for use in this invention are those which are derived from the condensation of aromatic, cycloaliphatic, and aliphatic diols with aliphatic, aromatic and cycloaliphatic dicarboxylic acids. Illustrative of useful aromatic diols, are those having from about 6 to about  
20 24 carbon atoms. Such aromatic diols include bis-(p-hydroxyphenyl)ether; bis-(p-hydroxyphenyl)thioether; bis-(p-hydroxyphenyl)-sulphone; bis(p-hydroxyphenyl)-methane; 1,2-(bis-(p-hydroxyphenyl)-ethane); 1-phenyl-bis-(p-hydroxy-phenyl)-methane; diphenyl-(bis-(p-hydroxyphenyl)-methane); 2,2-bis(4-hydroxy- dimethylphenyl) propane); 1,1- or 2,2-(bis(p-hydroxyphenyl)-  
25 butane); 1,1-dichloro-or 1,1,1-trichloro-2,2-(bis-(p-hydroxyphenyl)-ethane); 1,1-(bis-(p-hydroxyphenyl)-cyclopentane); 2,2-(bis-(p-hydroxyphenyl)-propane (Bisphenol A); 1,1-(bis-(p-hydroxyphenyl)-cyclohexane) (Bisphenol C); p-xylene glycol; 2,5-dichloro-p-xylylene glycol; p-xylene-diol; the fluoroalkyl and fluoroalkylene analogues of the above and the like, and blends thereof.  
30

Suitable cycloaliphatic diols include those having from about 5 to about 24 carbon atoms. Exemplary of such useful cycloaliphatic diols are 1,4-dihydroxy cyclohexane, 1,4-dihydroxy methylcyclohexane, 1,3-dihydroxy-cyclopentane, 1,5-dihydroxycycloheptane, 1,5-  
35 dihydroxycyclooctane, 1,4-cyclo-hexane dimethanol, 2,2-bis(4-hydroxycyclohexane)propane and the like, and blends thereof.

- 5 -

Useful and aliphatic diols include those having from about 2 to about 12 carbon atoms, with those having from about 2 to about 6 carbon atoms being particularly preferred. Illustrative of such preferred diol precursors are 1,2-ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,8-octanediol, 1,6-nonanediol, neopentyl glycol, pentyl glycol, 1,6-hexanediol, 1,4-butanediol, and the like, and blends thereof.

Cycloaliphatic diols and aliphatic diols are preferred for use. Propylene glycol, ethylene glycol, neopentyl diol, 1,4-dihydroxy methylcyclohexane, 1,4-butanediol and 2,2-bis(4-hydroxy cyclohexyl) propane are particularly preferred as diol precursors of polyesters for use in the conduct of this invention.

Suitable dicarboxylic acids for use as precursors in the preparation of useful polyesters are linear and branched chain saturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids and cycloaliphatic dicarboxylic acids. Polyesters containing up to about 80% repeat units of monomer containing both hydroxyl and carboxyl groups, such as hydroxybenzoic acid, vanillic acid, syringic acid and the like, may also be used in the practice of this invention. Illustrative of aliphatic dicarboxylic acids which can be used in this invention are those having from about 2 to about 50 carbons atoms, as for example, malonic acid, dimethylmalonic acid, succinic acid, itanoic acid, octadecylsuccinic acid, pimelic acid, adipic acid, trimethyladipic acid, sebacic acid, suberic acid, azelaic acid and dimer acids (dimerisation products of unsaturated aliphatic carboxylic acids such as oleic acid) and alkylated malonic and succinic acids, such as octadecylsuccinic acid, and the like, and blends thereof.

Illustrative of suitable cycloaliphatic dicarboxylic acids are those having from about 6 to about 15 carbon atoms. Such useful cycloaliphatic dicarboxylic acids include 1,3-cyclobutanedicarboxylic acid, 1,2-cyclopentanedicarboxylic acid, 1,3- and 1,4-cyclohexanedicarboxylic acid, 1,3- and 1,4-dicarboxymethylcyclohexane and 4,4-dicyclohexyldicarboxylic acid, and the like, and blends thereof.

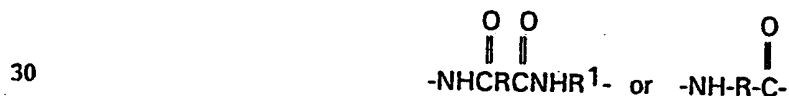
As is well known in the art, polyester compounds may be prepared by the condensation of a diol and either an aromatic dicarboxylic acid or a salt, such as dimethyl terephthalate, as illustrated in 68(11) Modern Plastics Encyclopedia '92, 41 - 48 (Mid October 1991). Illustrative of such useful aromatic carboxylic acids are terephthalic acid and isophthalic acid, 2,6- or 2,7-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4-

- 6 -

diphenylsulphone-dicarboxylic acid, 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)-indane, diphenyl ether 4,4-dicarboxylic acid bis-(p-carboxyphenyl) methane and the like. Of the aforementioned aromatic dicarboxylic acids based on a benzene ring such as terephthalic acid and isophthalic acid are preferred for use and amongst these preferred acid precursors terephthalic acid is particularly preferred. Copolymers and terpolymers prepared from mixtures of the above aromatic diacids may also be used.

In the most preferred embodiments of this invention, poly(ethylene terephthalate) ("PET"), poly(butylene terephthalate), poly(ethylene naphthalate) as well as copolymers and terpolymers thereof such as poly(ethylene/terephthalate/2,6-naphthalene dicarboxylate) and poly(tetramethylene/terephthalate/2,6-naphthalene dicarboxylate), are the polyesters of choice for both exterior layers 12 and 20. Among these polyesters of choice, poly(ethylene terephthalate) and the copolymers and terpolymers thereof are most preferred. The polyester used in layer 12 need not be the same polyester as used in layer 20, although the same materials are preferred.

Other polymers which may be employed in the exterior layer 20 include aliphatic polyamides or aliphatic/aromatic polyamides. As used herein, "aliphatic polyamides" are polyamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two aliphatic carbon atoms. Illustrative of these polyamides are those having recurring monomeric units represented by the general formula:



or a combination thereof in which R and R<sup>1</sup> are the same or different and are alkylene groups of at least about two carbon atoms, preferably alkylene groups having from about 2 to about 12 carbon atoms. Exemplary of such polyamides are polyamides formed by the reaction of diamines and diacids such as poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(hexamethylene azelamide)



- 7 -

(nylon 6,9), poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene azelamide) (nylon 10,9), and the like. Also illustrative of useful aliphatic polyamides are those formed by polymerization of amino acids and derivatives thereof, as for example lactams. Illustrative of these useful  
5 polyamides are poly(4-aminobutyric acid) (nylon 4), poly(6-aminohexanoic acid) (nylon 6, also known as poly(caprolactam)), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid)(nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic acid) (nylon 10), poly(11-amino-undecanoic acid) (nylon 11), poly(12-aminododecanoic acid) (nylon 12) and  
10 the like. Blends of two or more aliphatic polyamides may also be employed.

Copolymers formed from recurring units of the above referenced aliphatic polyamides can be used in the fabrication of the exterior layer 20. By way of illustration and not limitation, such aliphatic polyamide copolymers include caprolactam/hexamethylene adipamide copolymer  
15 (nylon 6/6,6), hexamethylene adipamide/caprolactam copolymer (nylon 6,6/6), trimethylene adipamide/hexamethylene azelaamide copolymer (nylon trimethyl 6,2/6,2), hexamethylene adipamide/hexamethylene-azelaamide/caprolactam copolymer (nylon 6,6/6,9/6) and the like. Preferred aliphatic polyamides for use in the practice of this invention are  
20 poly(caprolactam) and poly(hexamethylene adipamide), with poly(caprolactam) being the most preferred.

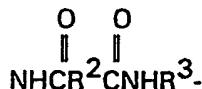
Aliphatic polyamides used in the practice of this invention may be obtained from commercial sources or prepared in accordance with known preparatory techniques. For example, polycaprolactam can be obtained from  
25 AlliedSignal Inc.

The number average molecular weight of the polyamide may widely vary. Usually, the aliphatic polyamide is of a "film-forming molecular weight", meaning a weight that is sufficiently high to form a free standing film but sufficiently low to allow melt processing of the blend into a film.  
30 Such number average molecular weights are well known to those of skill in the film forming art and are usually at least about 5,000 as determined by the formic acid viscosity method. In this method (ASTM D-789), a solution of 11 grams of aliphatic polyamide in 100 ml of 90% formic acid at 25°C is used. In the preferred embodiments of the invention, the number average  
35 molecular weight of the aliphatic polyamide ranges between about 5,000 to about 100,000, and in the particularly preferred embodiments it ranges between about 10,000 to about 60,000. Most preferred are those in which

- 8 -

the number average molecular weight of the aliphatic polyamide is from about 20,000 to about 40,000.

In the alternative, one exterior layer 20 may be formed from an "aliphatic/aromatic polyamide". As used herein, an "aliphatic/aromatic polyamide" is characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain where the carbonyl moieties are separated by aliphatic moieties having at least two carbon atoms and where the nitrogen groups are separated by aromatic moieties. Illustrative of these aliphatic/aromatic polyamides are those having recurring units of the formula:



in which  $R^2$  and  $R^3$  are different and are alkylene group having at least 2 carbon atoms (preferably having from 2 to about 12 carbon atoms) or arylene (preferably substituted or unsubstituted phenylene, alkylphenylene or dialkylphenylene and wherein the aliphatic moieties have from 1 to about 7 carbon atoms wherein permissible substituents are alkyl, alkoxy or halo), with the proviso that when  $R^2$  is arylene,  $R^3$  is alkylene and when  $R^2$  is alkylene,  $R^3$  is arylene or dialkylene phenylene. Exemplary of such polyamides are poly(hexamethylene isophthalamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(m-xylylene adipamide) (MXD6), poly(p-xylylene adipamide), poly(hexamethylene terephthalamide), poly(dodecamethylene terephthalamide), and the like.

Blends of two or more aliphatic/aromatic polyamides can also be used. Preferred aliphatic/aromatic polyamides for use in the fabrication of layer 20 are poly(hexamethylene isophthalamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(m-xylylene adipamide), poly(p-xylylene adipamide), poly(hexamethylene terephthalamide), and poly(dodecamethylene terephthalamide). More preferred aliphatic/aromatic polyamides are poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(m-xylylene adipamide), and poly(p-xylylene adipamide), and the most preferred aliphatic/aromatic polyamide is poly(m-xylylene adipamide).

Aliphatic/aromatic polyamides can be prepared by known preparative techniques or can be obtained from commercial sources.

The number average molecular weight of the aliphatic/aromatic polyamide may vary widely. Usually, the aliphatic/aromatic polyamide is of

- 9 -

a "film-forming molecular weight", again meaning a weight that is sufficiently high to form a free standing film and sufficiently low to allow melt processing of the blend into a film. Such number average molecular weights are well known to those of skill in the film forming art and are  
5 usually at least about 5,000 as determined by the formic acid viscosity method described above. In the preferred embodiments of the invention, the number average molecular weight of the aliphatic/aromatic polyamide is from about 5,000 to about 100,000, and in the particularly preferred  
10 embodiments is from about 10,000 to about 60,000. Most preferred are those in which the number average molecular weight of the aliphatic/aromatic polyamide is from about 20,000 to about 40,000.

Interior layer 16 may be comprised of either an ethylene-vinyl alcohol copolymer ("EVOH") or a blend of an aliphatic/aromatic polyamide and EVOH. Preferably interior layer 16 is comprised of the EVOH alone.

15 EVOH, whether used alone or in a blend in interior layer 16, preferably has an ethylene content of between about 27 mole percent to about 48 mole percent, more preferably between about 27 mole percent to about 44 mole percent, and most preferably between about 32 mole percent to about 38 mole percent. The EVOH further preferably has a density  
20 ranging between about 1.12 g/cm<sup>3</sup> to about 1.20 g/cm<sup>3</sup>, preferably about 1.19 g/cm<sup>3</sup>, and a melting temperature ranging between about 142°C to about 191°C, preferably about 183°C. EVOH can be prepared by known preparative techniques or can be obtained from commercial sources. For example, such ethylene vinyl alcohol components can be obtained from  
25 Morton Inc. or Evalca, Inc.

The aliphatic/aromatic polyamides and blends thereof suitable for use in the exterior layer 20 may also be used in the blend of interior layer 16.

The blend of interior layer 16 may be prepared by mechanically blending, such as in a drum tumbler, about 50% to about 95%, preferably about  
30 65% to about 85%, of the aliphatic/aromatic polyamide with about 5% to about 50%, preferably about 15% to about 35%, of EVOH at room temperature for about 30 minutes. Most preferably, about 70% to about 80% of the aliphatic/aromatic polyamide is mechanically blended with about 20% to about 30% of EVOH copolymer. As used herein, all percentages are by weight  
35 unless otherwise indicated. Preferably, the aliphatic/aromatic polyamide is MXD6.

- 10 -

Layers 14 and 18 are comprised of a modified polyolefin adhesive. The adhesive used in layer 14 need not be the same adhesive as used in layer 18. The polyolefins which may be used to form the modified reaction product suitable for the present invention include crystalline or crystallizable poly( $\alpha$ -olefins) and their copolymers, wherein the  $\alpha$ -olefin monomers have between about 2 and about 6 carbon atoms. Non-limiting examples of suitable polyolefins include low, medium or high density polyethylene, linear low density polyethylene, polypropylene, polybutylene, polybutene-1, polypentene-1, poly-3-methylbutene-1, poly-4-methylpentene-1, polyhexene, and copolymers and blends thereof. Of these, preferred polyolefins are polyethylene, polypropylene, polybutylene, and copolymers and blends thereof, with polyethylene being most preferred.

The modified polyolefins suitable for use in conjunction with the present invention include copolymers and graft copolymers of a polyolefin and a constituent having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof. The unsaturated polycarboxylic acids and anhydrides include maleic acid, maleic anhydride, fumaric acid, crotonic acid, citraconic anhydride, itaconic anhydride and the like. Preferred of these are anhydrides, of which the most preferred is maleic anhydride.

The preferred modified polyolefin comprises between about 0 and about 15 weight percent of the functional moiety, based on the total weight of the modified polyolefin, selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof. More preferably, the functional moiety comprises between about 0.1 and about 12 weight percent, most preferably between about 5 and about 10 weight percent.

The modified polyolefin of the present invention preferably further comprises between about 0 to about 1 weight percent, based on the total weight of the modified polyolefin, of vinyl acetate. More preferably, the modified polyolefin comprises between about 0 and about 0.5 weight percent of vinyl acetate; most preferably, between about 0.1 and about 0.3 weight percent.

The modified polyolefins suitable for the present invention can be obtained from commercial sources, e.g. from Du Pont under the tradename "CXA". Alternatively, such modified polyolefins may be produced in accordance with the processes known to the art, including but not limited to the processes described in U.S. Patent Nos. 3,481,910; 3,480,580;

- 11 -

4,612,155 and 4,751,270. In performing the graft-polymerization of unsaturated carboxylic acid and anhydride to polyolefin, there have been utilized various methods for initiating the grafting polymerization process such as  $\gamma$ -ray, x-ray or high-speed cathode ray irradiation processes, and a free radical initiator process. The reaction of the polyolefin with an unsaturated polycarboxylic acid or an anhydride in the presence of a free radical (e.g. a peroxide) is the most widely used method of the grafting process. The method of using peroxide is advantageous since no special equipment or device is required for initiating the graft polymerization reaction although the method suffers from non-specificity and less than optimal grafting efficiency. Examples of the peroxides employable include benzoyl peroxide, tert-butyl peroxybenzoate, cumene hydroperoxide and azo compounds, such as azo-bis(isobutyronitrile). U. S. Patent No. 4,612,155 discloses a grafting process employing such a radical initiator that obtains the grafting yield of 50 - 90 percent under favorable circumstances. U.S. Patent No. 4,751,270 discloses more specialized radical initiators that attain up to 100 percent grafting efficiency and improve grafting specificity of the functional moiety to polyolefins.

Graft polymerization reaction is generally performed by standard graft polymerization techniques known in the art, such as heating a mixture of a polyolefin, a monomer of the functional moiety and a radical initiator, after mixing those or in mixing procedure, to a temperature at which polyolefin becomes molten, under kneading of the mixture. Alternatively, the above-stated compounds are dissolved or suspended in a appropriate solvent to perform the graft polymerization reaction.

The modified polyolefins suitable for use in the present invention may also contain at least one thermoplastic elastomer such as ethylene/propylene rubber, ethylene/1-butene rubber, butyl rubber, butadiene rubber, styrene/butadiene rubber, ethylene/butadiene rubber, isopropene rubber, isobutylene or the like. A preferred thermoplastic elastomer is ethylene/propylene rubber. Such thermoplastic elastomers may also be modified with a constituent having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof, such as by the method described above in conjunction with modified poly ( $\alpha$ -olefin).

In addition to layers 12, 14, 16, 18, and 20 for film 10, the film may include one or more optional layers, provided that layer 16 is positioned

- 12 -

between layers 12 and 20 in film 10. Illustrative of such additional optional layers are polymeric layers formed of homopolymers and copolymers formed from  $\alpha$ -unsaturated monomers, such as, for example, polyolefin homopolymers such as polyethylene and polypropylene, polyvinyl alcohol, ethylene/propylene copolymer, ethylene/vinyl alcohol copolymer and blends thereof. Additional layers also include other adhesive tie layers to bond various layers together. Non-limiting examples of other optional polymeric layers and adhesive or tie layers which can be used in the film laminate of the present invention are disclosed in U.S. Patent Nos. 5,055,355; 3,510,464; 3,560,461; 3,847,845; 5,032,656; 3,585,177; 3,595,740; 4,284,674; 4,058,647; and 4,254,169.

The film of this invention can be formed by any conventional technique for forming films, including extrusion lamination and coextrusion. In the most preferred method, the film is formed by coextrusion. For example, the material of the individual layers 12, 14, 16, 18, and 20 for film 10, as well as any optional layers, are fed into infeed hoppers of the extruders of like number, each extruder handling the material for one of the layers. Preferably if more than one layer of the film is comprised of the same material, then that material is extruded into its respective layers from a single extruder. For example, if both exterior layers are comprised of PET, then the PET is extruded into layers 12 and 20 from a single extruder, with the extrudate being split into the respective individual layers after it passes through both the single extruder and a feedblock co-extrusion adaptor, and then emerges from the co-extrusion die. Most preferably, three extruders are used, one being for the EVOH or EVOH-aliphatic/aromatic layer, one for the adhesive layer, and one for the PET layers.

The melted and plasticated streams from the individual extruders are fed into a single manifold co-extrusion die. While in the die, the layers are juxtaposed and combined, then emerge from the die as a single multiple layer film of polymeric material. After exiting the die, the film is cast onto a first controlled temperature casting roll, passes around the first roll, and thence onto a second controlled temperature roll, which is normally cooler than the first roll. The controlled temperature rolls largely control the rate of cooling of the film after it exits the die. In a preferred embodiment of this invention where layers 12 and 20 are PET, layers 14 and 18 are polyethylene modified with maleic anhydride and vinyl acetate, and layer 16 is EVOH, typical operating temperatures for the first and second controlled

- 13 -

temperatures rolls are approximately 275°F (135°C) and 230°F (110°C), respectively.

In another method, the film forming apparatus may be one which is referred to in the art as a "blown film" apparatus and includes a multi-  
5 manifold circular die head for bubble blown film through which the plasticized film composition is forced and formed into a film "bubble". The "bubble" is ultimately collapsed and formed into a film.

Processes of coextrusion to form film and sheet laminates are generally known in the art.

10 The films of this invention may be of any thickness desired and include those which have thicknesses typically less than about 5 mils (127  $\mu$ m). Preferably, the films have a thickness of from about 1 mil (25  $\mu$ m) to about 3 mils (75  $\mu$ m); more preferably the films have a thickness of from about 1 mil (25  $\mu$ m) to about 1.5 mils (38  $\mu$ m). While such thicknesses are  
15 preferred as providing a readily flexible film, it is to be understood that other film thicknesses may be produced to satisfy a particular need and yet fall within the scope of the present invention.

The films of this invention may optionally be stretched or oriented in any direction if so desired using methods known to those of skill in the art.  
20 In such a stretching operation, the film may be stretched in either: 1) the direction coincident with the direction of movement of the film being withdrawn from the casting roll, also referred to in the art as the "machine direction"; 2) the direction which is perpendicular to the machine direction, and referred to in the art as the "transverse direction" where the resulting  
25 film is "uniaxially" oriented; or 3) the machine direction as well as in the transverse direction, where the resulting film is "biaxially" oriented.

Typically for use in the present invention, the oriented film formed from the composition of the invention are preferably produced at draw ratios of from about 3:1 to about 6:1, and preferably at a draw ratio of from about 3:1 to  
30 about 4:1. The term "draw ratio" as used herein indicates the increase of dimension in the direction of the draw. Therefore, a film having a draw ratio of 2:1 has its length doubled during the drawing process. Generally, the film is drawn by passing it over a series of preheating and heating rolls. The heated film moves through a set of nip rolls downstream at a faster rate  
35 than the film entering the nip rolls at an upstream location. The change of rate is compensated for by stretching in the film.

- 14 -

Typical process and range of conditions for monoaxially oriented polyamide films are disclosed, for example, in U.S. Patent No. 4,362,385. The film laminate of the present invention can be biaxially oriented using blown tube apparatus, or a tenter frame apparatus, and can either be sequentially or simultaneously oriented biaxially. The film laminate of the present invention can also be embossed after orientation.

The films of this invention can be used for any purpose for which films can be used. One noteworthy characteristic of the films of this invention is that they exhibit excellent gas barrier properties, particularly oxygen barrier properties, at 90% relative humidity (RH). Oxygen barrier resistance may be measured using a film having a gauge of 0.60 mils and the procedure of ASTM D-3985 using an OX-Tran 1050 cell manufactured by Modern Controls Inc. operated at 23°C.

In general, using the aforesaid method, the films of this invention have an oxygen transmission rate ( $O_2TR$ ) at 90% RH equal to or less than about  $0.04 \text{ cm}^3 / 100 \text{ in}^2 / 24 \text{ hrs/Atm}$  at 23°C. The superior oxygen barrier properties of the films of this invention makes them especially useful in food packaging applications.

Another noteworthy characteristic of the films of the present invention is its ability to withstand retorting. The retortable properties of the films of the present invention were tested by manufacturing an article, such as a pouch or a lid for a container, comprised of a layer of the film of the present invention sandwiched between an interior layer of polypropylene and an exterior layer of polyester. The article was sealed, then placed into an autoclave or other pressurized chamber at approximately 119°C to about 123°C for approximately 30 minutes. While in this chamber, the article undergoes the retorting process with the steam present therein. The films of the present invention displayed superior retortable properties, as determined by their ability to retain their original optical appearance and structural integrity.

In practical use, for example, a film with superior retortable properties is especially useful in packaging applications for food which needs to be sterilized and/or which will subsequently be heated for a "heat and serve" product. Typically, the food is placed into the pouch or container, such that the food contacts the polypropylene layer of the pouch or lid, respectfully, and the pouch or container is then sterilized. Such a sealed



- 15 -

pouch or container often is in a form suitable for subsequent heating or cooking by the consumer.

Several examples are set forth below to illustrate the nature of the invention and the manner of carrying it out. However, the invention should not be considered as being limited to the details thereof.

#### EXAMPLE I

A co-extruded film was made from two exterior layers of PET produced by AlliedSignal Inc. sandwiching an interior layer formed of ethylene vinyl alcohol ("EVOH") obtained from Evalca, Inc. The PET had an intrinsic viscosity of .95. The EVOH had an ethylene content of 32 mole percent, a density of 1.19 g/cm<sup>3</sup> and a melting temperature of 183 °C. A modified polyolefin adhesive tie layer obtained from Mitsui Petrochemicals Co. under the tradename "Admer AT-469D", was coextruded between each exterior layer of PET and the EVOH layer.

The PET, EVOH, and the adhesive tie layers therebetween were co-extruded to form a five layer co-extruded film. The PET was extruded through a 3½ inch (88.9 mm) diameter Davis Standard Extruder having a temperature profile of Zone 1-505°F, Zone 2-510°F, Zone 3-515°F, Zone 4-525°F, Zone 5-525°F and adapter Zone 1-525°F, corresponding respectively to temperatures of 263 °C, 265 °C, 268 °C, 274 °C, 274 °C and 274 °C. The extruder operated with a screw speed of 25 rpm, a motor drive amperage of 70 amps, a barrel pressure of 1100 psig (7.6 MPa), a melt temperature of the PET at 535 °F (280 °C), and an extruder output of 150 pounds per hour (68 kg/hr).

The EVOH was extruded through a 2 inch (50.8 mm) diameter Wellex extruder. The extruder had a temperature profile which included Zone 1-350°F, Zone 2-450°F, and Zone 3-455°F and adapter Zone 1-460°F, corresponding to temperatures of 177 °C, 232 °C, 235 °C, and 238 °C, respectively. The operating conditions of the extruder included a screw speed of 70 rpm, a motor drive amperage of 21 amps, a melt temperature of 486 °F (252 °C), and an extruder output of 70 pounds per hour (32 kg/hr).

The adhesive was extruded through a 1.25 inch (32 mm) diameter Wellex extruder. The extruder had a temperature profile which included Zone 1-450°F, Zone 2-475°F, and Zone 3-500°F and adapter Zone 1-500°F, corresponding to temperatures of 232 °C, 246 °C, 260 °C, and 260 °C, respectively. The operating conditions of the extruder included a screw

- 16 -

speed of 60 rpm, a motor drive amperage of 5 amps, a melt temperature of 484 °F (251 °C), and an extruder output of 15 pounds per hour (6.8 kg/hr).

The extrudate from the three extruders was fed through a feed block coextrusion adaptor manufactured by the Johnson Plastic Corporation and operating at an adaptor temperature of Zone 1- about 460 to 525 °F, and Zone 2-about 460 to 525 °F (corresponding to about 238 °C to about 274 °C). The flat cast die temperatures were operated at about 525 °F (274 °C). The coextruded film was then cast on a roll at a temperature of about 275 °F (135 °C) and a rotation speed of 25 feet/min (7.6 m/min), followed by a cooling roll at a temperature of about 230 °F (110 °C) and a rotation speed of 25 feet/min (7.6 m/min). The total extrusion output was 235 pounds per hour (107 kg/hr) and the line speed was about 95 feet per minute (28.9 m/min).

The film was oriented monoaxially. The film was passed to a slow stretch roll at a temperature of about 200°F (94 °C) and a rotation speed of about 25 feet/min (7.6 m/min), then to a fast stretch roll at a temperature of about 200°F (94 °C) and a rotation speed of 100 feet/min (30.5 m/min), and then to a heat set roll at a temperature of about 240 °F (115 °C) and a rotation speed of 97 feet/min (29.5 m/min). The line speed was 95 feet per minute (29 m/min) and the draw ratio was 4.0.

Two films, "Film 1" and "Film 2", were fabricated. Film 1 had an average gauge of 1.1050 mils and Film 2 had an average gauge of 1.1700 mils. In place of the "Admer AT-469D" adhesive of Film 1, Film 2 incorporated a different modified polyolefin adhesive layer obtained from Du Pont, Inc. under the tradename "CXA3101", which was coextruded between each exterior layer of PET and the EVOH layer. The films and other physical characteristics are set forth in the following Table I.

- 17 -

TABLE I

PROPERTY	FILM AND VALUE			
	FILM 1		FILM 2	
	MD <sup>1</sup>	TD <sup>2</sup>	MD	TD
Tensile, Modulus, psi ( MPa)	832700 (5700)	336400 (2304)	763900 (5230)	337100 (2310)
Yield, psi ( MPa)	-	8742 (60)	-	8402 (58)
Yield Elongation %	-	7.533	-	7.821
Strength, psi ( MPa)	34870 (240)	9415 (67)	34440 (236)	9312 (64)
Elongation %	38.70	390.1	50.09	400.0
Tear, Elmendorf gms/layer	90.4	1600	93.6	1600
Tear, Graves gms/mil	612.4	1236	619.5	1299
Average Dimensional Stability (%) 350°F (177 °C), 10 Min.	-16.5	-6.5	-15.9	-6.2

<sup>1</sup> MD = machine direction<sup>2</sup> TD = transverse direction**EXAMPLE II**

5 A series of experiments were carried out to test the oxygen permeability of the film laminates prepared in Example I. The films were tested for oxygen permeability using the Ox-Tran 1050 cell operated at 23°C. The procedure used was that disclosed in ASTM D-3985. The oxygen permeability was measured in cubic centimeters per 100 inch square

10 per 24 hours per Atm at 23°C and 90% relative humidity.

The results are set forth in the following Table II.

TABLE II

FILM	O <sub>2</sub> TR (90% RH)
Film 1	0.0432
Film 2	0.0435

It can be seen that Films 1 and 2 have excellent oxygen barrier properties.

The films produced in Example I were subjected to a standard retorting process at temperatures of about 250°F (121°C) for approximately 30 minutes. Both films retained their original optical appearance and structural integrity.

Thus, it can be seen that the addition of EVOH sandwiched by adhesive tie layers to a polyester-layered composition produces a film having improved gas impermeability characteristics in comparison to those of polyester alone, which is well-known in the art to range between about 3.0 to about 4.0 cm<sup>3</sup>/100in<sup>2</sup>.

Moreover, due to EVOH's inability to withstand moisture and thus its "non-retortable" characteristics, it would be expected that if a greater than nominal amount of EVOH were added to the polyester composition, the composition would degrade during the retortability tests. However, as demonstrated by the Example II, the addition of a significant amount of EVOH to the interior layer of a polyester-layered composition further improved the composition's overall oxygen impermeability characteristics without reducing its retortability characteristics or physical properties. Thus, the EVOH becomes retortable, while the gas impermeability characteristics of the overall composition is enhanced.

It can be seen that the present invention provides films with excellent physical and oxygen barrier properties, as well as exhibits enhanced heat resistant properties to withstand the rigors of retorting conditions.

- 19 -

**WHAT IS CLAIMED IS:**

1. A retortable film comprised of:

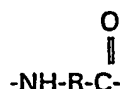
a) a first exterior layer comprised of polyester;

b) a second exterior layer comprised of a polymer selected  
5 from the group consisting of aliphatic polyamides, aliphatic/aromatic  
polyamides, polyesters and blends and copolymers thereof;

c) an interior layer comprised of a component selected from  
the group consisting of ethylene vinyl alcohol copolymer and a blend of  
ethylene vinyl copolymer and an aliphatic/aromatic polyamide; and

d) an adhesive layer positioned between each exterior layer  
10 and said interior layer.

2. A film according to claim 1 wherein said aliphatic polyamide is  
selected from the group consisting of polyamides having recurring  
monomeric units of the formula:



or a combination thereof wherein:

R and R<sup>1</sup> are the same or different and are alkylene having at least  
about 2 carbon atoms.

3. A film according to claim 2 wherein said aliphatic polyamide is  
selected from the group consisting of poly(hexamethylene adipamide),  
poly(4-aminobutyric acid), poly(caprolactam), poly(7-aminoheptanoic acid),  
30 caprolactam/hexamethylene adipamide copolymer, and hexamethylene  
adipamide/caprolactam copolymer.

4. A film according to claim 1 wherein said polyester is selected  
from the group consisting of poly(ethylene terephthalate), poly(butylene  
terephthalate), poly(ethylene naphthalate) and copolymers and terpolymers  
thereof.

5. A film according to claim 1 wherein each of said adhesive  
layers is independently comprised of a modified poly( $\alpha$ -olefin) having about 2  
to 6 carbons, and about 0 to about 15 weight percent, based on the total

- 20 -

weight of said modified poly( $\alpha$ -olefin), of a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides.

5 6. A film according to claim 5 wherein said functional moiety is selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, crotonic acid, citraconic anhydride, and itaconic anhydride.

7. A film according to claim 6 wherein said modified poly( $\alpha$ -olefin) further comprises about 0 to about 1 weight percent, based upon the total weight of said modified poly( $\alpha$ -olefin), of vinyl acetate.

10 8. A film according to claim 1 wherein said interior layer is a blend of an ethylene vinyl alcohol copolymer and poly(m-xylylene adipamide).

9. A film according to claim 8 wherein said interior layer contains, based upon the total weight of interior layer, about 65% and 85% of said poly(m-xylylene adipamide) blended with about 15% to 35% of said  
15 ethylene vinyl alcohol copolymer.

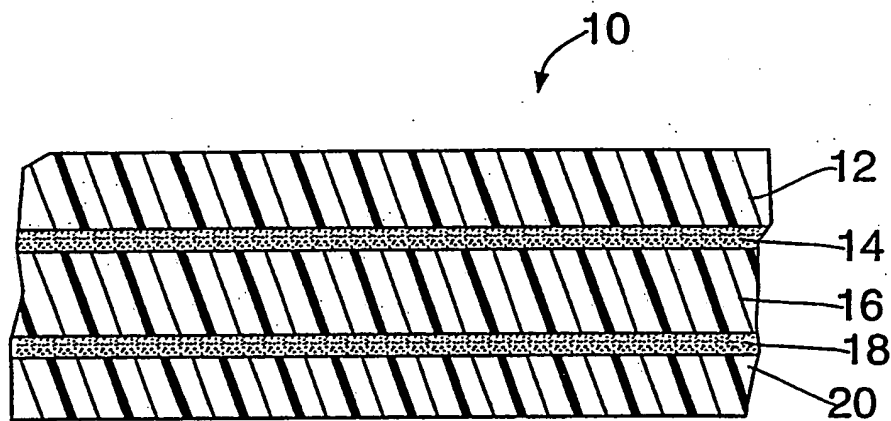
10. A film according to claim 1 having an oxygen permeability at 90% relative humidity equal to or less than about  $0.04 \text{ cm}^3/100 \text{ in}^2/\text{Atm}$ .

11. A film according to claim 1 wherein said interior layer is comprised of ethylene vinyl alcohol copolymer.

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1/1

FIG. 1



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 95/07508

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 27/08, B32B 27/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO, A1, 9507180 (ALLIEDSIGNAL INC.), 16 March 1995 (16.03.95), the whole document	1-11
X	EP, A1, 0515795 (KURARAY CO, LTD.), 2 December 1992 (02.12.92), page 8, line 11-17; page 9, line 20-30, 39-40	1-11
A	EP, A2, 0306675 (KURARAY CO., LTD.), 15 March 1989 (15.03.89), page 8, line 26-34, example 1, claim 9	1-11

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

### \* Special categories of cited documents:

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*Z\* document member of the same patent family

Date of the actual completion of the international search

2 October 1995

Date of mailing of the international search report

24 -10- 1995

Name and mailing address of the International Searching Authority



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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US 95/07508

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EPOQUE, PAJ/JPO, JP1253442, KURARAY CO LTD: "GAS BARRIER MULTILAYER PACKAGE", 891009  -----	1-11

# INTERNATIONAL SEARCH REPORT

SA 172206

28/08/95

International application No.

PCT/US 95/07508

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO-A1-	9507180	16/03/95	NONE		
EP-A1-	0515795	02/12/92	JP-A-	5193076	03/08/93
			US-A-	5221566	22/06/93
EP-A2-	0306675	15/03/89	DE-D, T-	3886631	11/05/94
			JP-A-	1027941	30/01/89
			US-A-	4929482	29/05/90